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CATALYTIC REDUCTION OF SULFUR DIOXIDE BY CARBON MONOXIDE. (PART I. EFFECT OF GAS CONCENTRATIONS ON THE CONVERSION OF SULFUR DIOXIDE)

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CATALYTIC REDUCTION OF SULFUR DIOXIDE BY CARBON MONOXIDE --(PART I. EFFECT OF GAS CONCENTRATIONS ON THE CONVERSION OF SULFUR DIOXIDE)-- Ichisankatanso ni yoru nisankaiwo no sesshoku kangen --(Dai 1 po. Nisankaiwo henkaritsu ni taisuru gasu nodo no eikyo)--

by

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Research Report 71109
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Thermodynamics and kinetics of catalytic sulfur dioxide reduction by carbon monoxide in the gas mixture consisting of sulfur dioxide, carbon monoxide, carbon dioxide and nitrogen were investigated in this paper.

(1) The maximum conversion of sulfur dioxide was obtained at 400-500°C by using bauxite as a catalyst.

(2) The catalysts having oxides of metals such as iron, copper, calcium and silver in each alumina showed high activity on the sulfur dioxide reduction by carbon monoxide.

(3) The equilibrium conversion of sulfur dioxide by carbon monoxide increased with the increase of the reaction temperature and carbon monoxide concentration but decreased with the increase of carbon

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dioxide concentration.

(4) The reaction rate by bauxite catalyst had first order dependence on sulfur dioxide concentration and carbon monoxide concentration but was affected inversely by carbon dioxide concentration at temperatures above 600°C.

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1. Introduction

Research and development on the desulfurization methods of stack discharge are advancing in many countries such as Japan, Germany, the United States, France, etc. but there is yet to emerge a practically applicable procedure.

The direct reduction method of sulfur dioxide by carbon monoxide converts sulfur dioxide into sulfur according to

$$SO_2 + 2CO = \tfrac{1}{2}S_2 + 2CO_2.$$

In connection with this reduction method, R. Lepsoe of Canada [1] has presented a thermodynamic discussion of the reduction reaction of sulfur dioxide. He also considered the exhaust gas from a furnace and compared the activity of activated alumina catalysts (not clear concerning other types of catalyst) under the condition of interaction temperature 250 - 700°C and contact time 60 seconds [2]. P. R. Ryason et al of the United States [3], on the other hand, considered a case of reaction temperature 540°C and contact time 0.35 seconds and compared the activity of various catalysts (catalysts with copper, silver and palladium and silicone catalysts with copper, silver, nickel and magnesium) by using a gas mixture containing SO_2 (0.5%), CO, CO_2 and N_2. More recently, a

research project is under way at MIT [4] in search for a catalyst by using a gas mixture not containing oxygen. No details are yet available. Furthermore, Sanaa E. Khalafalla et al [5] are reporting on the effects of iron content in the iron-alumina catalysts on the removal efficiency of SO_2 at 500 - 600°C. In this research, a gas mixture consisting of SO_2, CO and N_2 has been used.

The purpose of the present paper is to present the results of our research on the possibility of direct reduction by carbon monoxide of the sulfur dioxide contained in the exhaust gas from a combustion furnace. By means of small, fixed-floor type equipment and by using a gas mixture consisting of SO_2, CO, CO_2 and N_2, the catalytic effects (mainly of bauxite), the reaction speed and the chemical equilibrium were studied under the conditions of reaction temperatures 100 - 900°C and contact time less than 0.30 seconds.

2. Method of measurement

2.1. Apparatus and method

The reaction speed between SO_2 and CO was obtained inside a gas mixture SO_2-CO-CO_2-N_2 by using the apparatus shown in Fig. 1 and under various conditions.

The quartz reaction tube used in the experiment has an inner radius of 27 cm and length 10.5 cm.

The gas mixture was prepared by passing fixed amounts of SO_2 (0.5%, nitrogen balanced), CO (10.0%, nitrogen balanced), CO_2 (99.9%) and N_2 from their respective pressure containers. In order to produce a uniform mixture, the gas was passed through a glass orifice of inner radius 0.04 cm.

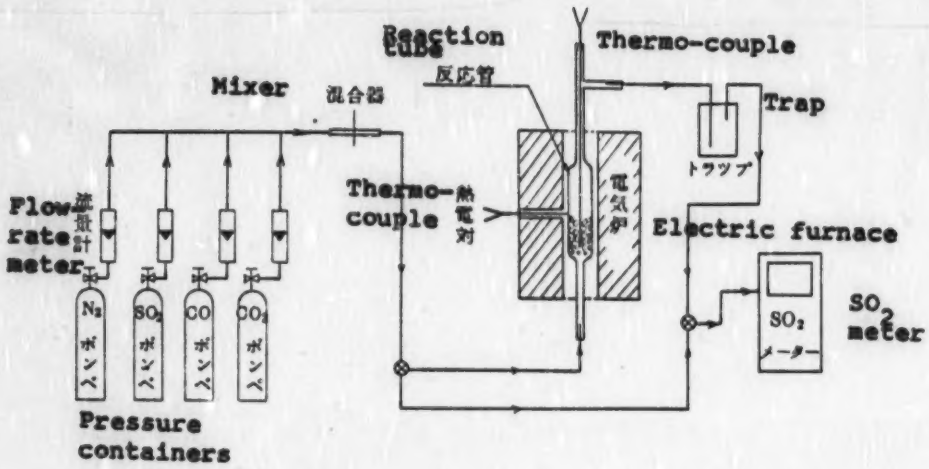


Fig. 1. Apparatus

The SO_2 and CO of the gas mixture interact with each other while passing through the layer of catalyst in the reaction tube so that SO_2 is reduced. The sulfur dioxide concentration consequently decreases. The sulfur dioxide concentration is measured before and after the reaction by means of an electric conductivity type SO_2 meter. The conversion rate is obtained from this difference in the SO_2 concentration. The concentrations of CO and CO_2 are measured by gas chromatography method.

The following experimental conditions were used:

i) SO_2 concentration 0.17 - 0.19%

ii) CO concentration 0.4 - 1.6%

iii) CO_2 concentration 0 - 15%

iv) Flow rate of gas 0.25 - 1.5 ℓ/min

v) Reaction temperature 100 - 900°C

vi) Amount of catalyst 0 - 20 mℓ

The air speed when the catalyst is present is about 1000 - 30000 h^{-1} (NTP). The contact time in this case is about 0.02 - 0.30 seconds.

2.2. Catalysts

As catalysts, we used activated alumina of grain size 2.0 - 4.0 mm (γ -alumina; neobid D), alumina with metal (neobid D + iron, silver, copper, calcium, magnesium) and bauxite.

The activated alumina was heated at 700°C for three hours.

The alumina catalysts with metal were prepared by soaking pieces of activated alumina (heated at 700°C for 3 hours) in nitric salt solutions of the metals for 24 hours and then heated at 550°C for 3 hours.

The bauxite catalysts were prepared by heating at 550°C for 3 hours.

The chemical compositions of the activated alumina and bauxite are shown in Table 1

Table 1. Chemical compositions of the activated alumina and bauxite

	Chemical components (%)					
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	P_2O_5	C
Activated alumina	90	10	trace	–	–	–
Bauxite	809	53	102	32	014	015

2.3. Measurement of the surface area of the catalyst and the volume of infinitesimal holes

The surface area of the catalyst was measured by the BET method while the volume of infinitesimal holes was measured by the high pressure mercury method.

3. Experimental results

3.1. Cases without catalyst

Reduction experiments were conducted by passing mixtures of SO_2 (0.17 - 0.19%) and CO (0.4 - 1.6%) through the unfilled reaction tube at the rate of 0.25 ℓ /min and at 500 - 900°C. Fig. 2 shows the obtained results.

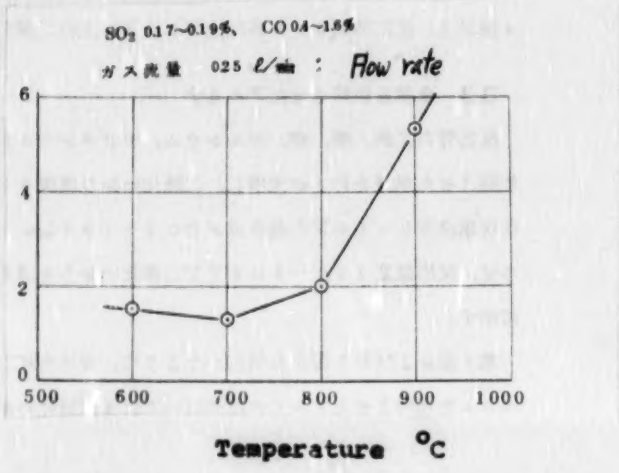


Fig. 2. SO_2 conversion rate when no catalysts are present

As seen in Fig. 2, the conversion of SO_2 by CO is nearly zero if no catalyst is present. Even when the reaction temperature was 900°C, the SO_2 conversion was no more than 5%. The SO_2 conversion remained nearly unchanged if the CO concentration was increased to 2 - 8 times that of SO_2.

3.2. Activated alumina

The reaction tube was filled with about 20 mℓ of alumina and the gas mixture prepared similarly to the above cases were passed through at the rate of 0.25 - 0.80 ℓ /min (air speed 1000 - 3000 h^{-1}). Fig. 3 shows the results of the experiment thus conducted at the designated

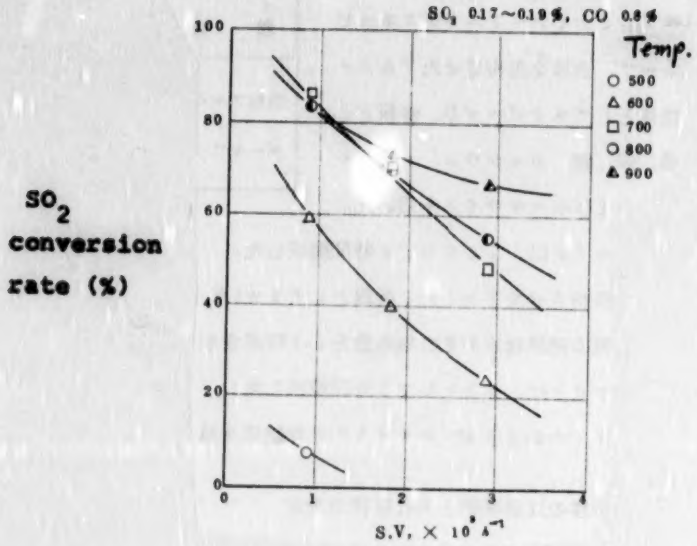


Fig. 3. SO_2 conversion rate when activated alumina is used as catalyst

temperatures.

Figs. 2 and 3 show that the conversion rate is markedly increased by filling the reaction tube with activated alumina. Fig. 3 also shows that the conversion rate is increased when the reaction temperature, the reaction time and the CO concentration are increased. If the reaction temperature is over 700°C, the CO concentration is more than 4 times that of SO_2 and the reaction time is over 0.19 seconds, the conversion rate is seen to be greater than 80%.

3.3. Alumina with metals

This time, the reaction tube is filled with about 4 mℓ of a catalyst made by attaching 5 wt % of metals (iron, silver, copper, calcium and magnesium) to activated alumina. A gas mixture consisting

of SO_2 (0.18 - 0.19%), CO (0.9%) and CO_2 (0 - 10%) is passed through it at the rate of 0.3 - 1.5 ℓ/min (air speed 5000 - 30000 h^{-1}) and at 200 - 900°C. Figs. 4 - 6 show the results of this series of reduction experiments.

As is clear from Figs. 4 and 5, the SO_2 conversion rate becomes, in all cases except when magnesium is added to the alumina, about 3 times that when alumina alone is used as catalyst. This is independent of whether or not CO_2 is present in the gas mixture. In the case of alumina with iron having the largest catalytic effect, the SO_2 conversion rate was over 80% when the CO concentration was 4 times that of SO_2 and the reaction time was over 0.13 seconds.

Fig. 6 shows that the SO_2 conversion rate reaches its maximum value at 400 - 600°C if alumina with metals is used as catalyst. The conversion

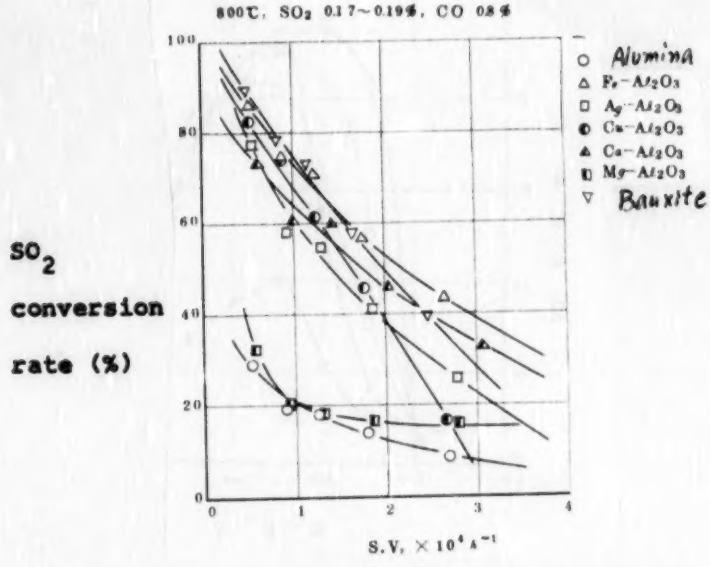


Fig. 4. Effects of metals on the SO_2 conversion rate (CO: 0.8%)

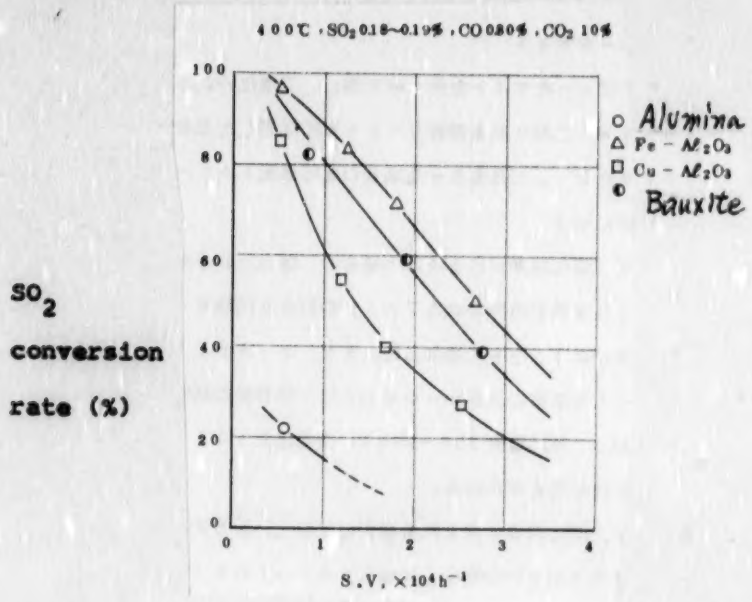


Fig. 5. Effects of metals on the SO_2 conversion rate (CO: 0.8%, CO_2: 10%)

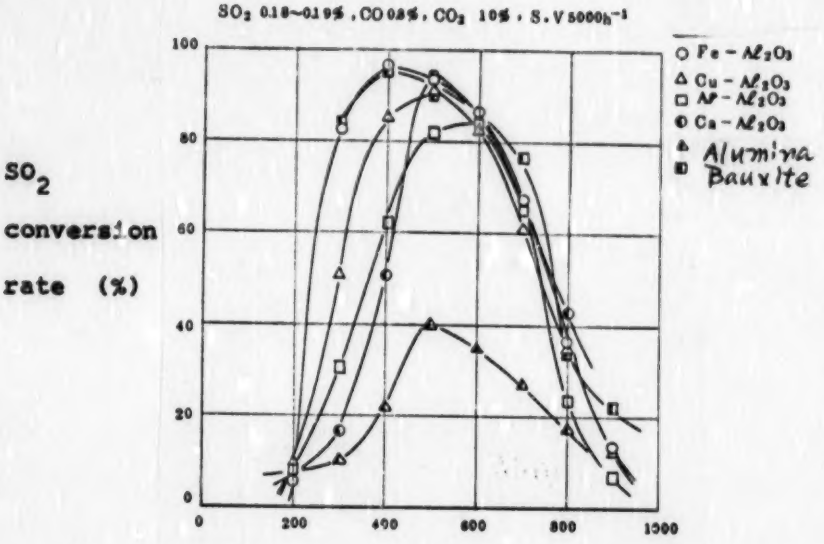


Fig. 6. Effects of metals on the SO_2 conversion rate (CO: 0.8%, CO_2: 10%)

rate decreases as the reaction temperature is raised above 600°C or lowered below 400°C.

R. Lepsoe [2] has compared the efficiency of various kinds of catalyst including alumina under the conditions of reaction temperature 250 - 700°C and reaction time 60 seconds but no details have been reported. Sanaa E. Khalafalla et al [5], on the other hand, have used a catalyst with alumina and red iron ore and investigated the effects of iron content in the catalyst under the reaction conditions of temperature 500°C, the SO_2 concentration 4.7%, the CO concentration 10% (nitrogen balanced) and the gas flow rate 0.5 - 2.0 ℓ/min. According to their report, the activity reaches its maximum value when the iron content is 43%.

A nitrogen balanced gas mixture consisting of SO_2 (0.5%), CO (2.0%) and CO_2 (10%) was used by P. R. Ryason, et al [3]. The reaction temperature was 540°C and the reaction time was 0.35 seconds (air speed 10^4 h^{-1}). At MIT [4], an oxygen-free gas mixture was used with the reaction temperature below 500°C. Both groups have reported that the copper-alumina catalyst is the most efficient. Their experimental conditions are somewhat different from ours but as far as materials with high activities are concerned the results are quite similar.

3.4. Bauxite

The reaction tube is filled with about 4 mℓ of bauxite and a gas mixture consisting of SO_2 (0.18 - 0.19%), CO (0.4 - 1.6%) and CO_2 (0 - 15%) is passed through it at 100 - 900°C and at 0.3 - 2.0 ℓ/min (air speed 5000 - 30000 h^{-1}). Figs. 7 - 10 show the SO_2 conversion rates in these experiments.

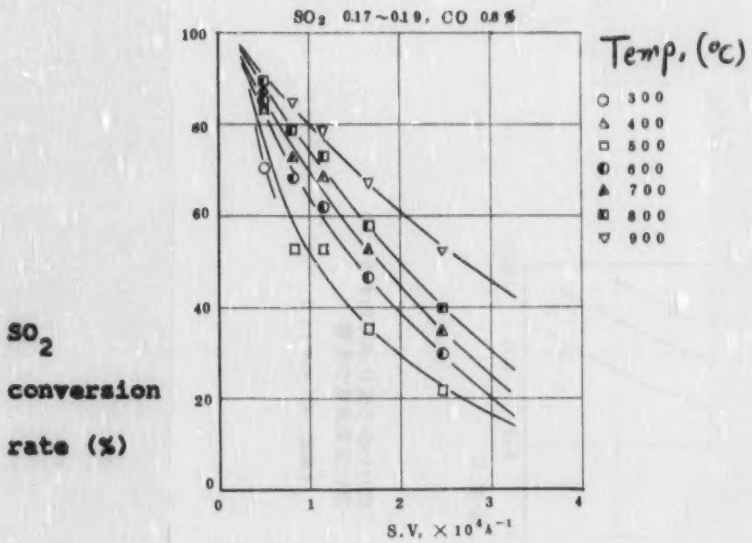


Fig. 7. SO_2 conversion rate when bauxite is used (CO: 0.8%)

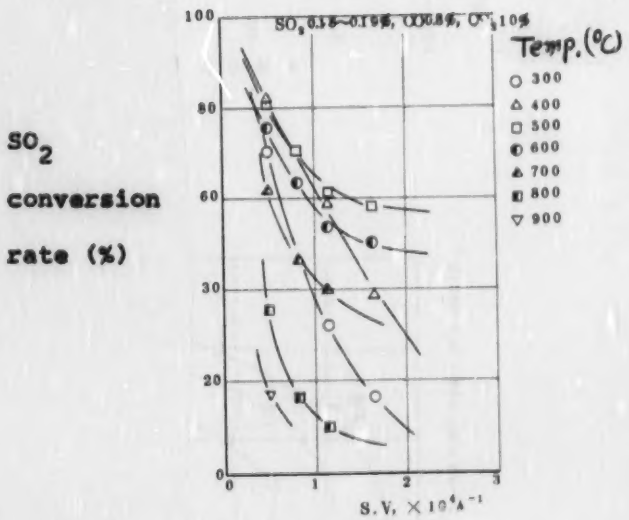


Fig. 8. SO_2 conversion rate when bauxite is used (CO: 0.8%, CO_2: 10%)

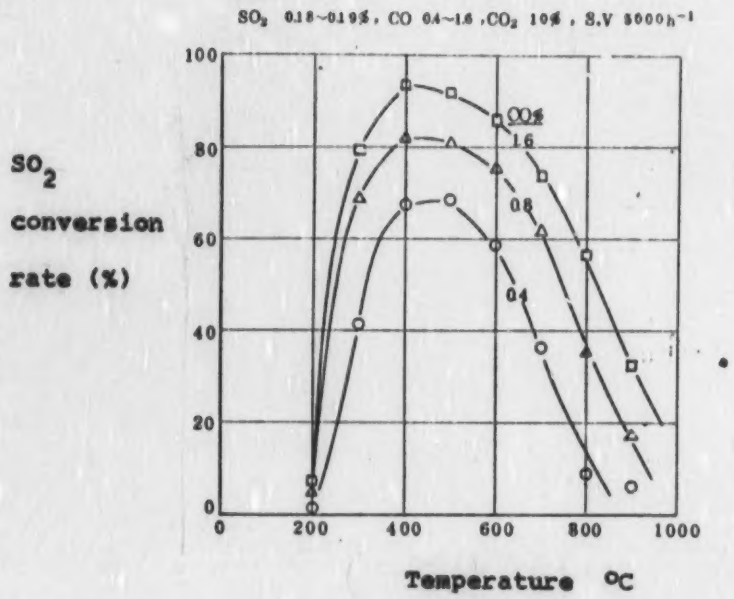


Fig. 9. Effects of CO concentration on SO_2 conversion rate

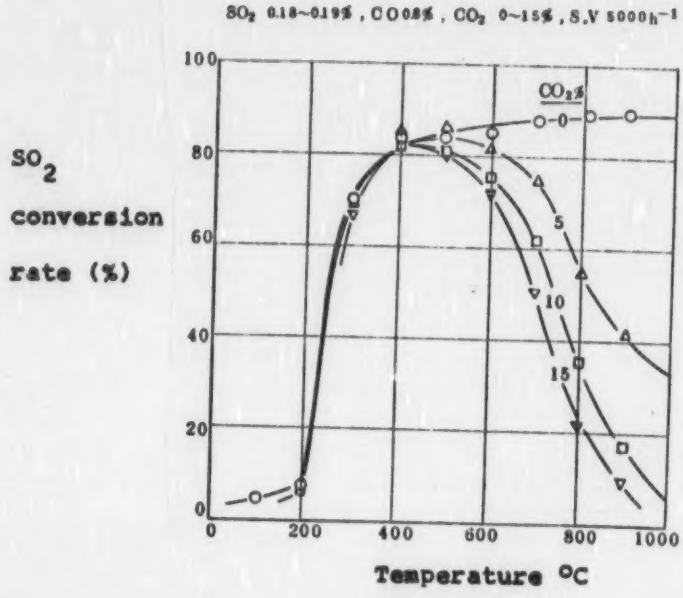


Fig. 10. Effects of CO concentration on SO_2 conversion rate

Fig. 7 shows the SO_2 conversion rate when the gas mixture is free of CO_2. As in the cases with alumina and alumina with metals, the conversion rate increases as the CO concentration and the reaction temperature are increased and the air speed is decreased. Furthermore, bauxite is found to be just as active as the most active alumina-plus-metal catalyst. When the CO concentration is over 4 times that of SO_2, the reaction temperature is 700 - 900°C and the air speed is less than 10000 h^{-1}, the SO_2 conversion rate is over 70%.

Figs. 8 - 10 show the cases when the gas mixture does contain CO_2. The temperature dependence of the conversion rate is similar to the case of alumina-plus-iron, reaching a maximum at 400 - 500°C and decreasing when the reaction temperature is raised above 600°C or decreased below 300°C. It also decreases when the CO concentration is lowered and the CO_2 concentration and the air speed are increased.

With bauxite as catalyst, the SO_2 and CO_2 concentrations respectively around 0.18 - 0.19% and 10 - 15% and the reaction temperature in the range 300 - 800°C, and SO_2 conversion rate over 60% was obtained under the following conditions.

Temp. (°C)	CO concentration (%)	Contact time (sec)
300	0.8	0.20
	1.6	0.15
400	0.4	0.14
	0.8	0.08
500	0.4	0.14
	0.8	0.07
600	0.4	0.15
	0.8	0.10
700	0.8	0.13
800	1.6	0.12

4. Discussion

4.1. Chemical equilibrium in the reaction between SO_2 and CO

The reaction between SO_2 and CO can be expressed as

$$SO_2 + 2CO = \tfrac{1}{2}S_2 + 2CO_2 \qquad (1)$$

At the same time, the reaction

$$\tfrac{1}{2}S_2 + CO = COS \qquad (2)$$

can also take place.

According to R. Lepsoe [1], the temperature dependence of the free energy differences ΔF_1° and ΔF_2° between the generating and reacting systems of the equations (1) and (2) is expressed as

$$\Delta F_1^\circ = -51760 + 2.75\,\ln T - 2.8\times10^{-3}T^2 - 3.1\times10^{-7}T^3 + 8.02T \qquad (3)$$

$$\Delta F_2^\circ = -22500 + 21.0T \qquad (4)$$

and the equilibrium constants of the reactions (1) and (2) are

$$K_1 = \frac{[S_2]^{1/2}[CO_2]^2}{[SO_2][CO]^2} \qquad (5)$$

$$K_2 = \frac{[COS]}{[S_2]^{1/2}[CO]} \qquad (6)$$

where $[SO_2]$, $[CO]$, $[S_2]$, $[CO_2]$ and $[COS]$ are the equilibrium concentrations of the gases.

The relationship between K and ΔF° is expressed as

$$\log K = \frac{-\Delta F^\circ}{2{,}303RT} \qquad (7)$$

Consequently, we obtain by substituting (3) and (4) into (7)

$$\log K_1 = \frac{11300}{T} - 1.375 \log T + 6 \times 10^{-4} T - 7 \times 10^{-8} T^2 - 1.77 \quad (8)$$

$$\log K_2 = \frac{4920}{T} - 4.6 \quad (9)$$

where $\triangle F^\circ$: The difference in free energy between the generating and reacting systems (cal/mol)

R : Gas constant (cal/deg mol)

T : Absolute temperature ($^\circ$K).

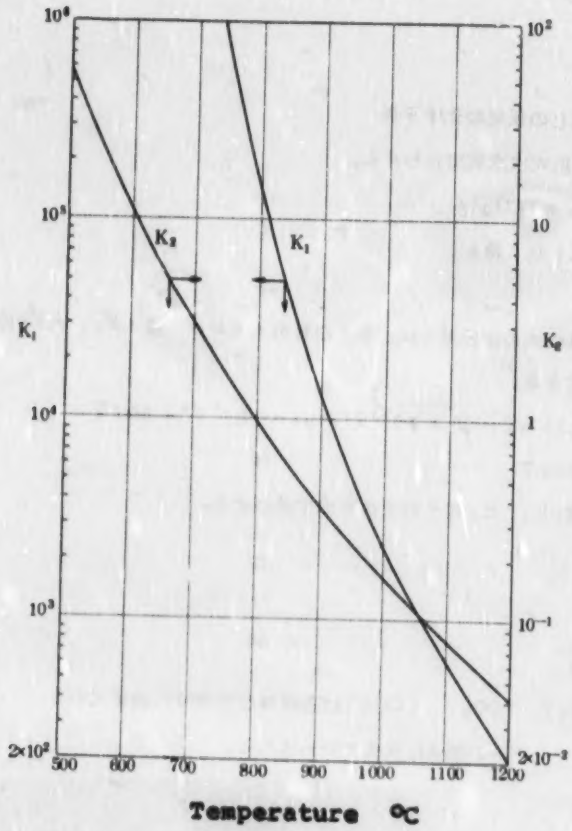
Fig. 11 shows the temperature dependence of K_1 and K_2 expressed by (8) and (9).

4.1.1. Gas composition and SO_2 conversion rate in equilibrium

(1) When CO_2 is not present before reaction:

An example of SO_2 conversion rate in an equilibrium state is shown in Fig. 12. As can be observed, the conversion rate increases as the reaction temperature and the CO concentration are increased. This figure as well as Figs. A1 - 3 (see Appendix) show that SO_2 conversion rates over 90% can theoretically be obtained under 900°C if the CO concentration is twice that of SO_2 and under 1250°C if the CO concentration is 4 times that of SO_2.

The amount of generated COS is considered to be about 10 ppm, according to Fig. 13 and the calculation of gas composition shown in



$$SO_2 + 2CO = \tfrac{1}{2}S_2 + 2CO_2$$

$$K_1 = \frac{(S_2)^{1/2}(CO_2)^2}{(SO_2)(CO)^2}$$

$$\tfrac{1}{2}S_2 + CO = COS$$

$$K_2 = \frac{(COS)}{(S_2)^{1/2}(CO)}$$

Fig. 11. Relationship between equilibrium constants and temperature

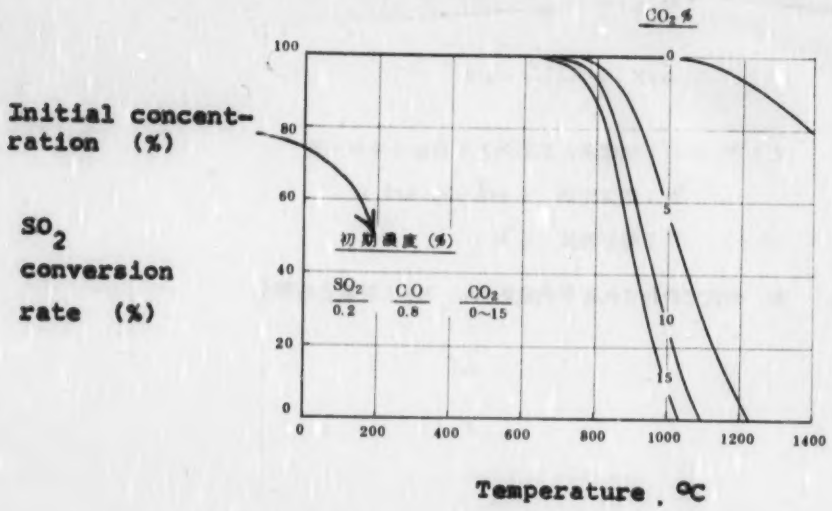


Fig. 12. SO_2 conversion rate in equilibrium states

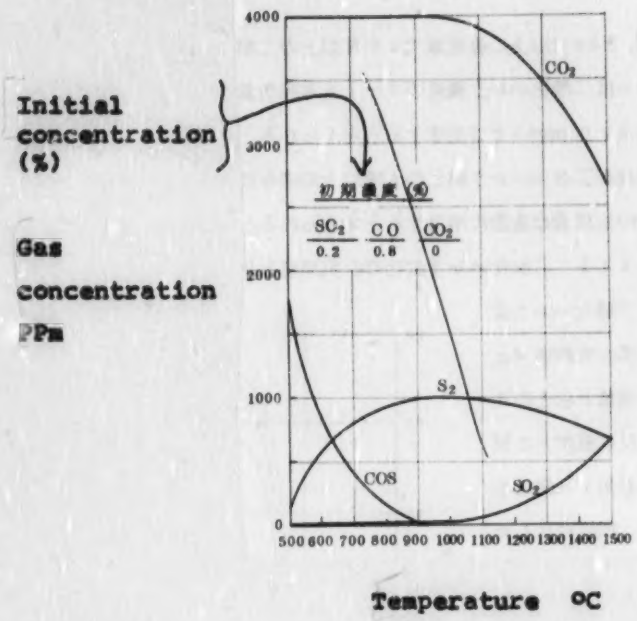


Fig. 13. Gas composition in equilibrium (CO: 0.8%)

APPENDIX (Figs. A4-6), if the CO concentration is twice that of SO_2 and the reaction temperature is 500 - 1000°C. If the CO concentration is 4 times that of SO_2 and the reaction temperature is over 1000°C, the generated amount will also be about 10 ppm. Below 1000°C, the generated amount is seen to vary rapidly with temperature.

(2) When CO_2 is contained in the gas mixture before reaction:

Fig. 12 also shows examples of the SO_2 conversion rate when CO_2 is present in the gas mixture prior to the beginning of the reaction. The SO_2 conversion rate is seen to increase rapidly as the reaction temperature and the CO_2 concentration are decreased and the CO concentration is increased.

The exhaust gas from combustion of heavy oil contains 12 - 15% of CO_2. According to Fig. 12 and Figs. A1 - 3, the reaction temperature must theoretically be below 780°C when the CO concentration is twice that of SO_2 if an SO_2 conversion rate greater than 60% is desired and the CO_2 concentration in the mixture is 10 - 15%. If the CO concentration is 4 times that of SO_2, the reaction temperature should be below 900°C and if the CO concentration is 8 times that of SO_2, the reaction temperature should be below 1000°C.

Fig. 14 shows an example of calculated gas composition in equilibrium states. If the gas contains 10 - 15% of CO_2, if the reaction temperature is over 800°C and if the condition is such that an SO_2 conversion rate over 60% can be attained, an amount corresponding to 2 - 15% of the SO_2 concentration (e.g. 40 - 300 ppm) if the initial SO_2

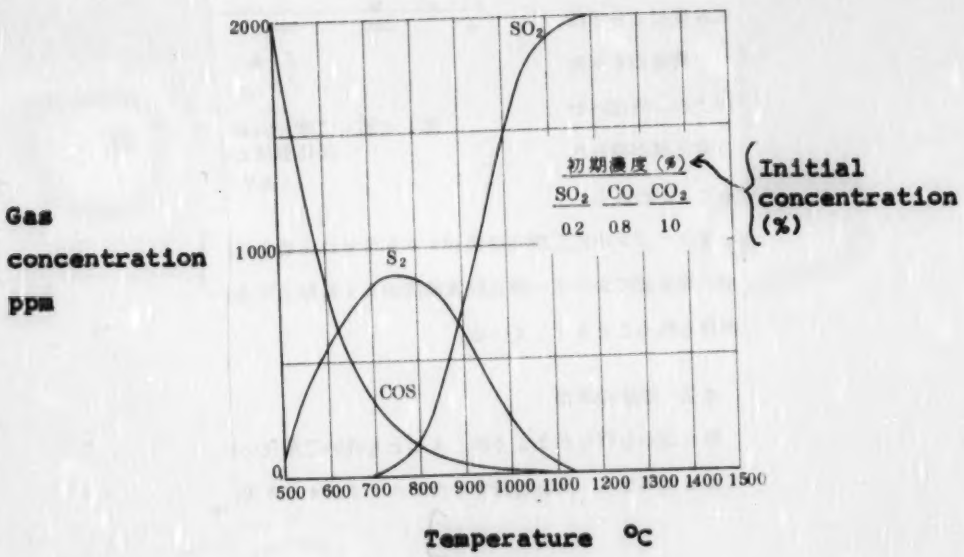


Fig. 14. Gas composition in equilibrium (CO: 0.8%, CO_2: 10%)

concentration is 2000 ppm) of COS may be expected to result. As shown in Fig. 14 as well as in Figs. A7 - 9, the produced amount of COS may be thought to decrease rapidly as the reaction temperature is dropped if the CO concentration is over 4 times that of SO_2 and the reaction temperature is below 800°C.

4.1.2. The measured and equilibrium values of the SO_2 conversion rate

Fig. 15 shows the relationship between the reaction temperature and the ratio of the measured (x) and the equilibrium (x_e) values of the SO_2 conversion rate. We learn from this figure that SO_2 conversion rates greater than 90% of the equilibrium value can be attained independently of the reaction temperature if CO_2 is absent in the gas mixture prior to the reaction and the CO concentration is over 0.8%.

If the gas mixture contains more than 10% of CO_2, the optimum reaction temperature is 400 - 500°C and SO_2 conversion rates greater

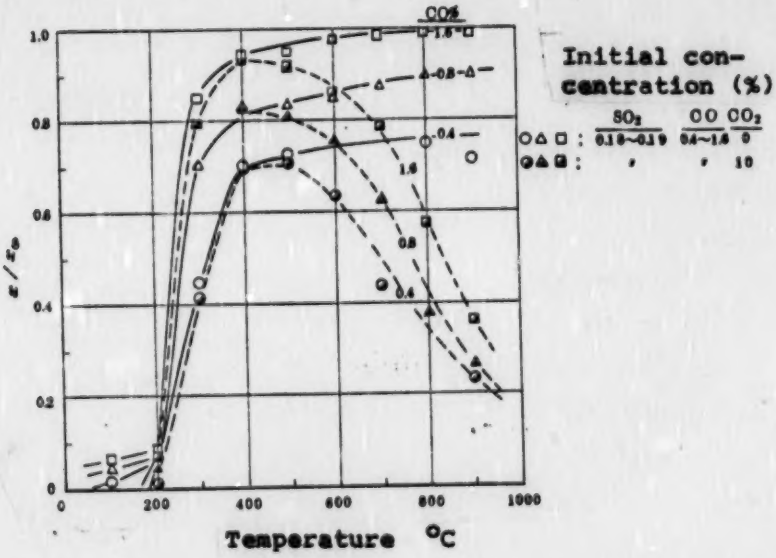


Fig. 15. Relationship between the reaction temperature and the ratio of the measured and equilibrium values of the SO_2 conversion rate

than 60% of the equilibrium value can be attained if the CO concentration is over 0.4%.

4.2. Activity of catalyst

As is clear from Fig. 6, the optimum range of reaction temperature which results in the maximum SO_2 conversion rates depends on the kind of catalyst used. It is 400°C for alumina with iron, 500°C for alumina with copper, 600°C for alumina with silver, 500°C for alumina with calcium, 500°C for activated alumina alone and 400°C for bauxite.

When metals are added to activated alumina, we can attain very high activities (in the order of iron, copper, calcium, silver). The SO_2 conversion rate increases by a factor of 2 - 4 compared to the case when activated alumina alone is used as catalyst. Magnesium, on the other hand, did not show any activity.

Table 2 shows the surface area and the hole volume of activated alumina and bauxite used as catalyst carrier.

Table 2. Surface area and hole volume of activated alumina and bauxite

	(a) mm	(b) g/cm³	(c) g/cm³	(d) m²/g	(e) cm³/g	(f) cm
Alumina	20~40	320	054	367	0682	43×10^{-7}
Bauxite	20~40	–	096	210	0264	45×10^{-7}

(a) Grain size, (b) True density, (c) Filled density, (d) Surface area, (e) Hole volume, (f) Average hole radius

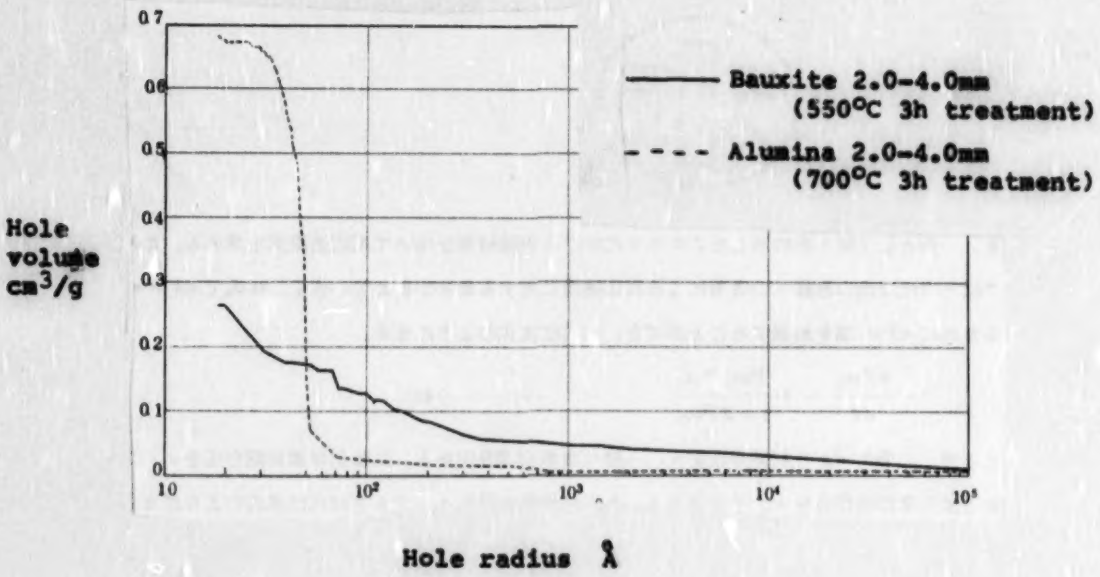


Fig. 16. Relationship between the hole radius and hole volume

Fig. 16 shows the relationship between the hole radius and the hole volume. The average hole radius is approximately the same for the two while the surface area and the hole volume are larger for activated alumina than for bauxite. Bauxite shows a high degree of activity comparable to that of alumina carrying iron. We may conclude that it is due to the iron contained in bauxite.

In summary, the reduction reaction of SO_2 by CO depends largely on the catalytic actions of activated metals.

4.3. Equation of reaction speed

The reaction between SO_2 and CO is expressed by (1) and the reaction

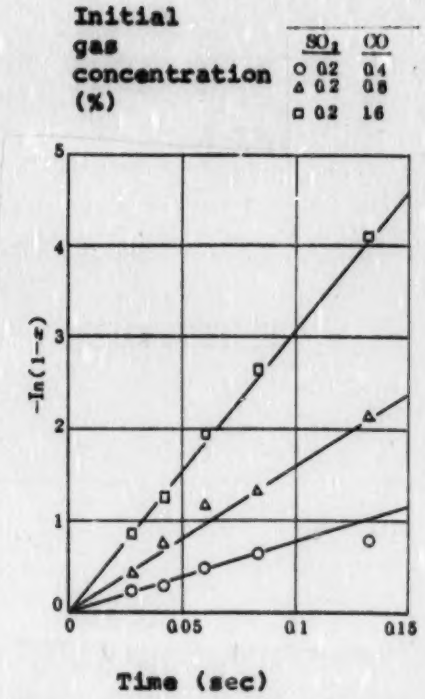


Fig. 17. Relationship between $-\ln(1 - x)$ and contact time (700°C)

speed when bauxite is used as catalyst was linear with respect to the partial pressure of SO_2 (see Fig. 17). Since the slope of the straight lines in this figure is proportional to the CO concentration, the reaction was linear also with respect to the partial pressure of CO. Below 300°C, however, a decrease in reaction speed was observed accompanied by the increase in the partial pressure of CO. Above 600°C, we also observed a decreasing tendency of the reaction speed when the partial pressure of CO_2 was increased.

We will now investigate the equation of reaction speed in the temperature range 300 - 900°C by assuming that the general equation of reaction speed is given by

$$-\frac{dP_{SO_2}}{dt} = k\frac{P_{SO_2}P_{CO}}{1+\alpha P_{CO}+\beta P_{CO_2}} \qquad (10)$$

where k : Reaction speed constant

P_{SO_2} : Partial pressure of SO_2 (atm)

P_{CO} : Partial pressure of CO (atm)

P_{CO_2} : Partial pressure of CO_2 (atm)

α, β : Constants.

As an example, let us derive an equation for reaction speed by using the experimental results at 700°C (Table 3). Since the effects of CO absorption by catalyst are very small on the reaction speed in this temperature range, we may set $\alpha P_{CO} = 0$ in (10). Thus, (10) becomes

$$-\frac{dP_{SO_2}}{dt} = k\frac{P_{SO_2}P_{CO}}{1+\beta P_{CO_2}} \qquad (11)$$

Table 3. Summary of experimental results (Bauxite, 700°C)

No. 実験番号	Gas flow rate ℓ/min (NTP)	Contact time sec	P_{SO_2} a $\times 10^{-3}$, atm	P_{CO} b $\times 10^{-3}$, atm	P_{CO_2} c $\times 10^{-3}$, atm	x	x_∞
701	0.3	0.132	1.88	3.98	0	0.543	0.981
702	0.5	0.083	1.87			0.466	
703	0.7	0.060	1.83			0.358	
704	1.0	0.042	1.72			0.256	
705	1.5	0.028	1.815			0.210	
706	0.3	0.132	1.80		99.6	0.361	0.824
707	0.3	0.132	1.91		149	0.268	0.781
708	0.3	0.132	1.88	7.97	0	0.884	0.998
709	0.5	0.083	1.88			0.729	
710	0.7	0.060	1.84			0.685	
711	1.0	0.042	1.78			0.523	
712	1.5	0.028	1.82			0.346	
713	0.3	0.132	1.80		49.8	0.750	0.998
714	0.5	0.079	1.84			0.625	
715	0.3	0.132	1.84		99.6	0.615	0.989
716	0.5	0.079	1.80			0.467	
717	0.7	0.057	1.80			0.400	
718	0.3	0.124	1.80		149	0.506	0.978
719	0.5	0.079	1.86			0.366	
720	0.7	0.057	1.78			0.258	
721	0.3	0.132	1.83	15.7	0	0.984	1.00
722	0.5	0.083	1.85			0.930	
723	0.7	0.060	1.86			0.855	
724	0.3	0.132	1.82		99.6	0.786	0.999
725	0.3	0.124	1.88		149	0.840	0.998

If the initial values of partial pressure are a, b and c for SO_2, CO and CO_2, respectively, and if t is the contact time, (11) becomes

$$\frac{dx}{dt} = k \frac{(1 - \frac{x}{x_\infty})(b - 2cx)}{1 + \beta(c + 2cx)} \qquad (12)$$

where x and x_∞ are as defined before. After integrating (12), we write the constant of reaction speed in the form

$$k = A + \beta B \qquad (13)$$

The experimental results of Table 3 are substituted into (13) and the relationship between A and B becomes as shown in Fig. 18. As is clear, the relationship can be expressed roughly in terms of a straight line and the values of k and β can be derived from the figure. Similar procedures were followed for different temperatures in the range 400 - 900°C.
In summary, the reaction speed in the temperature range 400 - 900°C increases proportionally to the partial pressures of SO_2 and CO but decreases as the partial pressure of CO_2 increases and it was expressible in the form (11).

The reaction speed at temperatures below 300°C was similarly analysed. In this temperature range, the effects of CO_2 absorption by the catalyst become very small and $\beta P_{CO_2} \fallingdotseq 0$ in (10). Thus, the reaction speed below 300°C increases in proportion with the partial pressures of SO_2 and CO but it is also affected by the CO absorption by the catalyst. Thus

$$-\frac{dP_{SO_2}}{dt} = k \frac{P_{SO_2} P_{CO}}{1 + \alpha P_{CO}} \qquad (14)$$

In summary, the reaction speed in the temperature range 300 - 900°C

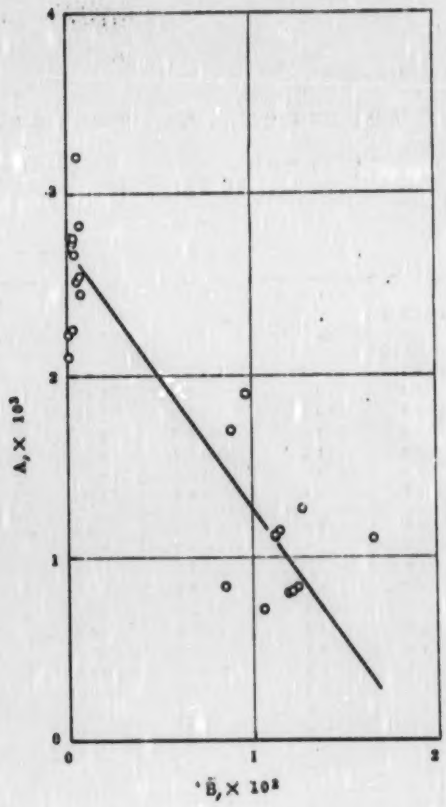


Fig. 18. Relationship between A and B (700°C)

can be expressed by (10), increasing in proportion with the partial pressures of SO_2 and CO but there is a deceleration, as the partial pressures of CO and CO_2 increase, caused by absorption by the catalyst.

This equation, furthermore, can be approximately written in the following ways depending on the temperature range.

(i) Below 300°C, the decelerating effects due to the SO_2 absorption by the catalyst become negligible. Hence (10) becomes (14).

(ii) Between 400 - 500°C, the decelerating effects due to the CO and CO_2 absorption by the catalyst become negligible. Therefore, (10) becomes

$$-\frac{d P_{SO_2}}{dt} = k P_{SO_2} P_{CO} \qquad (15)$$

(iii) Between 600 - 900°C, the decelerating effects due to the CO absorption by the catalyst become negligible. Hence (10) is approximated by (11).

4.4. Various effects on the reaction speed

4.4.1. Effects of reaction temperature

Fig. 19 shows the relationships among the reaction speed constant k, constants α and β and the reaction temperature. Bauxite is used as catalyst.

As is clear in this figure, the constant α which represents the CO absorption by the catalyst increases rapidly in the temperature range below 300°C while the constant β which represents the CO_2 absorption by the catalyst increases rapidly in the temperature range above 600°C, thus decelerating the reaction. In the temperature range 400 - 500°C, the decelerating effects due to the CO and CO_2 absorption by the catalyst are extremely small. In short, the reaction speed is influenced by CO in the lower temperature region and by CO_2 in the higher temperature region. The reaction speed as a whole, however, increases as the reaction temperature is raised.

According to Arrhenius, the reaction speed constant k may be written as

$$k = Ae^{-E_A/RT} \qquad (16)$$

The apparent activity energy E_A is approximately 3 Kcal/mol. Therefore,

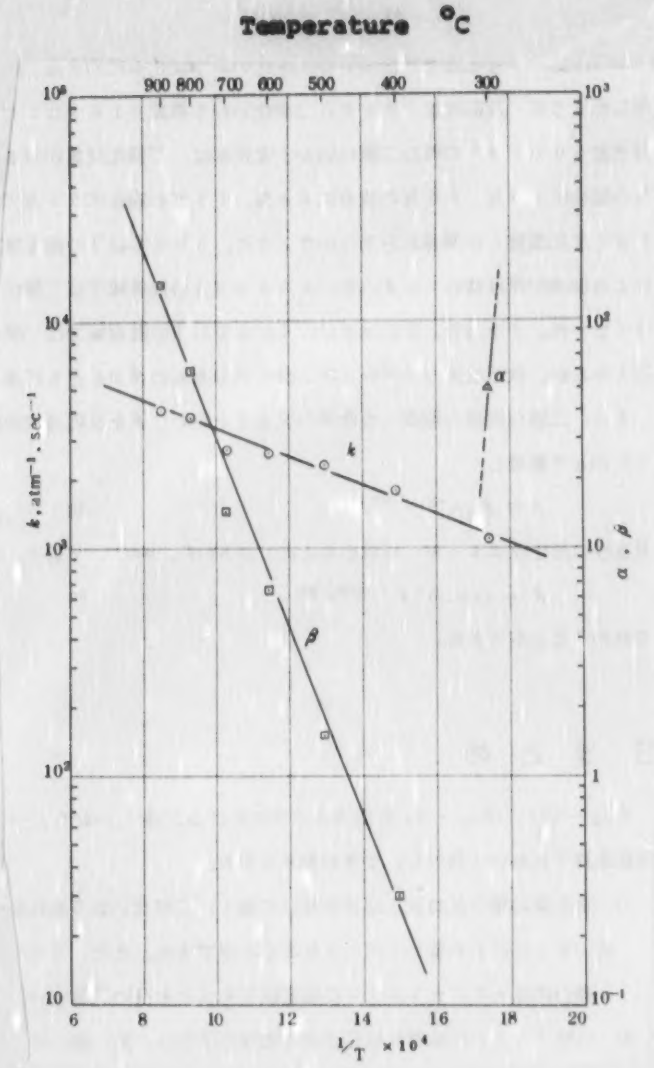


Fig. 19. Relationship between k, α and β .

$$k = 1.6 \times 10^4 e^{-3100/RT} . \qquad (17)$$

4.4.2. Effects of the CO concentration

The effects of the CO concentration on the SO_2 conversion rate were

already demonstrated in Fig. 9 for the case when bauxite was used as catalyst. When the reaction temperature was 700°C, the SO_2 concentration was 0.18 - 0.19%, the CO_2 concentration was 10% and the air speed was 5000 h^{-1}, the SO_2 conversion rate was 36%, 62% and 74%, respectively, corresponding to the CO density 0.4%, 0.8% and 1.6%. Furthermore, as is clear from the relationship between α and the reaction temperature shown in Fig. 19, the decelerating effects due to the CO absorption by the catalyst are large in the temperature range below 300°C but they become extremely small above 400°C. In other words, the reaction speed is lowered by the CO absorption by the catalyst if the reaction temperature is below 300°C but increases as the reaction temperature becomes higher and the CO concentration increases.

4.4.3. Effects of the CO_2 concentration

The effects of the CO_2 concentration on the SO_2 conversion rate were shown in Fig. 10 for the case when bauxite was used as catalyst. When the reaction temperature was 700°C, the SO_2 concentration was 0.18 - 0.19%, the CO concentration was 0.18% and the air speed was 5000 h^{-1}, then the SO_2 conversion rate was 88% in the absence of CO_2. It was 75, 62 and 51%, respectively, if the CO_2 concentration was 5, 10 and 15%. Furthermore, as is clear from the relationship between β and the reaction temperature shown in Fig. 19, the decelerating effects due to the CO_2 absorption by the catalyst were extremely small in the temperature range below 500°C but this effect became very large above 600°C. In other words, the reaction speed us lowered by the CO_2 absorption by the catalyst if the reaction temperature is above 600°C but increases if the reaction temperature is raised further and the CO_2 concentration decreases.

Here, too, the constant β representing the CO_2 absorption by the catalyst can be written in the Arrhenius' form:

$$\beta = \beta_0 e^{-E_A/RT} \qquad (18)$$

according to which the apparent activity energy E_A is approximately 1.9 Kcal/mol so that

$$\beta = 4.9 \times 10^5 e^{-19000/RT}. \qquad (19)$$

5. Summary

Under various experimental conditions, the reaction between SO_2 and CO was investigated in gas mixtures consisting of SO_2-CO-CO_2-N_2 and the following results have been obtained.

(1) If no catalyst is used, the reaction speed is extremely low and the SO_2 conversion rate is below 5%. The conversion rate can be raised drastically by using a catalyst. If a high concentration of CO_2 is contained in the gas mixture, the highest conversion rates are attained at 400 - 500°C.

(2) The catalytic activity of activated alumina increases when metals are added to it. Iron, copper, calcium and silver raise the activity while magnesium shows no activity. Bauxite shows a high degree of activity comparable to that of alumina with iron.

(3) The SO_2 conversion rate in an equilibrium state increases as the reaction temperature decreases and the CO concentration increases. It decreases as the CO_2 concentration increases. If the gas mixture contains 10 - 15% of CO_2, the SO_2 conversion rate theoretically becomes greater than 90% at temperatures below 620°C if the CO concentration is

twice that of SO_2, at temperatures below 800°C if the CO concentration is 4 times that of SO_2 and at temperatures below 900°C if the CO concentration is 8 times that of SO_2.

(4) If bauxite is used as catalyst, the reaction speed increases in proportion with the SO_2 and CO concentrations. Above 600°C, however, it decreases as the CO_2 concentration increases.

6. Acknowledgment

We benefited a great deal throughout this research from the useful advice of Mr. Kenichi Oda (Research consultant). We should like to thank him sincerely for his leadership.

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8. Appendix

Test calculation of the SO_2 conversion rate and the gas composition in an equilibrium state of the reduction reaction of SO_2 by CO:

1) Reaction equation and the constant of equilibrium (K)

$$2CO + SO_2 = 2CO_2 + \tfrac{1}{2}S_2 \qquad (1)$$

Initial concentration-- a, b, c, 0

Concentration at the time of equilibrium-- $a(1 - X)$, $(b - \frac{1}{2}aX)$, $(c + aX)$, $\frac{1}{2}aX$

$$K_1 = \frac{[CO_2]^2 [S_2]^{1/2}}{[CO]^2 [SO_2]} \qquad (2)$$

$$CO + \tfrac{1}{2}S_2 = COS \qquad (3)$$

Initial concentration: a, 0, 0

Concentration at the time of equilibrium: $a(1 - Y)$, $\frac{1}{2}aY$, aY

$$K_2 = \frac{[COS]}{[CO][S_2]^{1/2}} \qquad (4)$$

where X and Y are equilibrium conversion rates.

According to Lepsoe, the constants of equilibrium K_1 and K_2 are related with the reaction temperature by

$$\log K_1 = \frac{11300}{T} - 1375 \log T + 6 \times 10^{-4} T - 7 \times 10^{-8} T^2 - 177 \quad \cdots\cdots (5)$$

$$\log K_2 = \frac{4920}{T} - 46 \quad \cdots\cdots (6)$$

Fig. 11 shows these relationships.

ii) Gas concentrations at equilibrium:

	Initial concentration	Equilibrium concentration
$[CO]$	a	$a(1 - X - Y)$
$[SO_2]$	b	$b - \frac{1}{2}aX$

$[CO_2]$	c	c + aX
$[S_2]$	0	½a(X - 2Y)
[COS]	0	aY

Figs. A1 - 3 show examples of SO_2 conversion rate and Figs. A4 - 9 show examples of gas composition for cases a = 0.4, 0.8, 1.6%, b = 0.2% and c = 0, 5, 10, 15%.

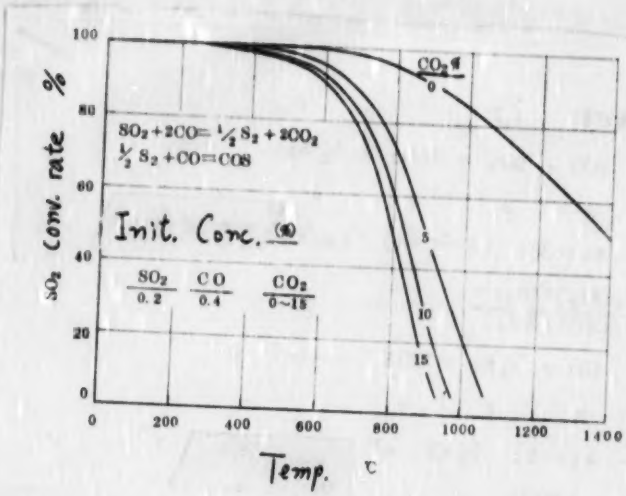

Fig. A1. SO_2 conversion rate in equilibrium state (CO: 0.4%)

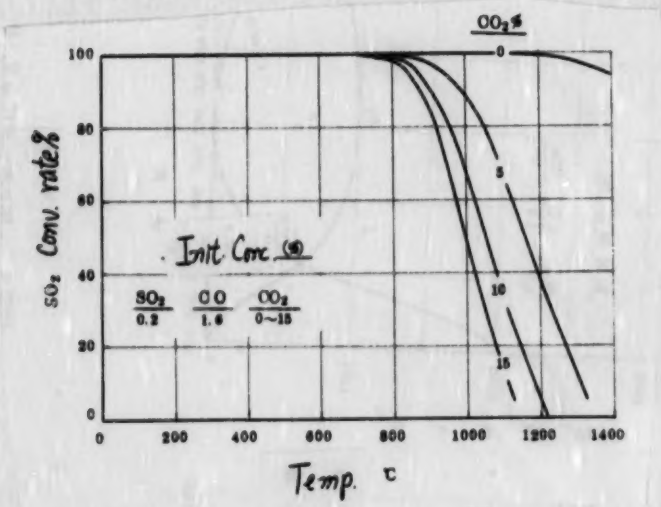

Fig. A2. SO_2 conversion rate in equilibrium state (CO: 0.8%)

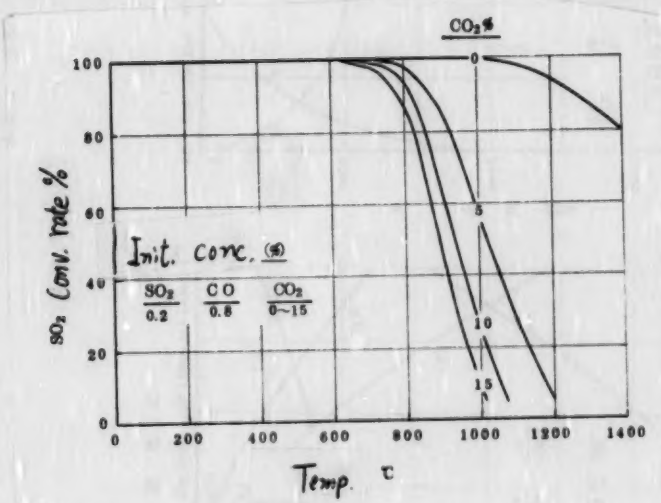

Fig. A3. SO_2 conversion rate in equilibrium state (CO: 1.6%)

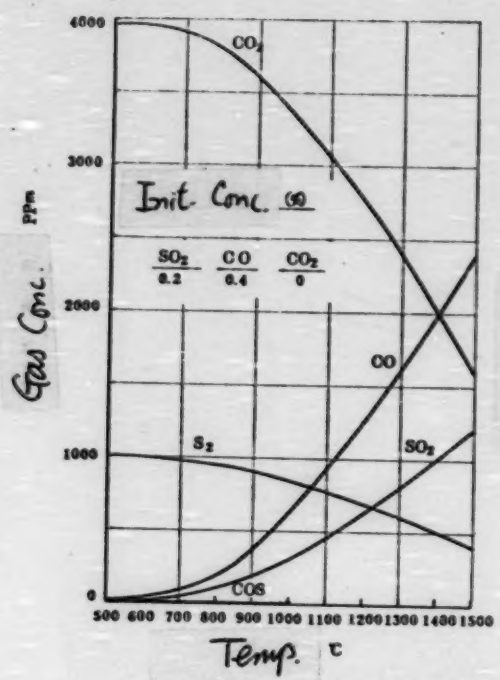

Fig. A4. Gas composition in equilibrium (CO: 0.4%)

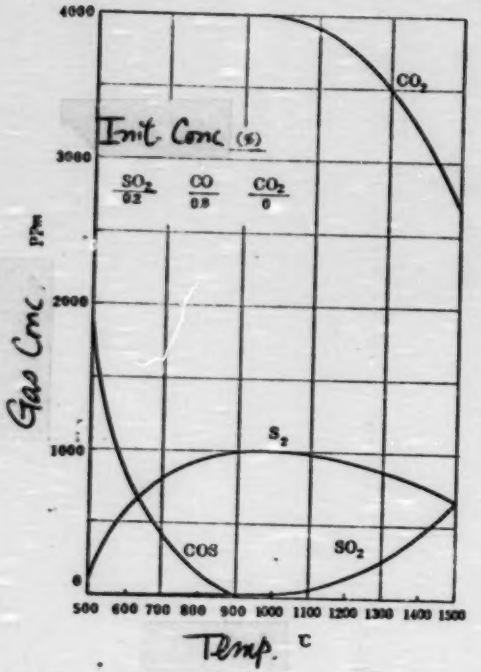

Fig. A5. Gas composition in equilibrium (CO: 0.8%)

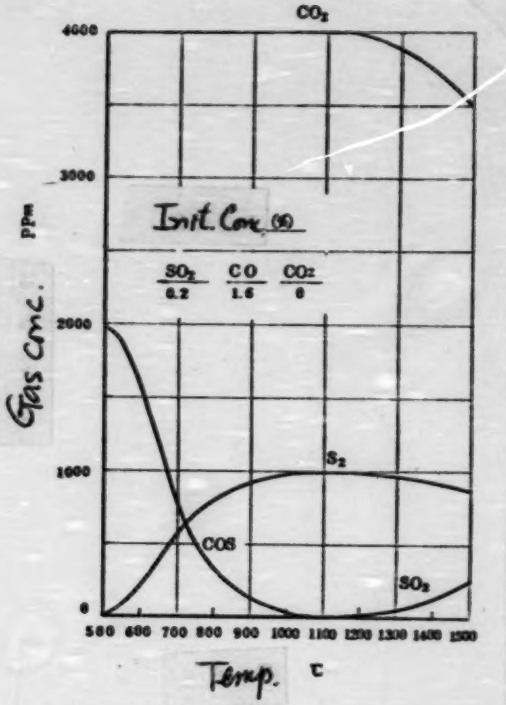

Fig. A6. Gas composition in equilibrium (CO: 1.6%)

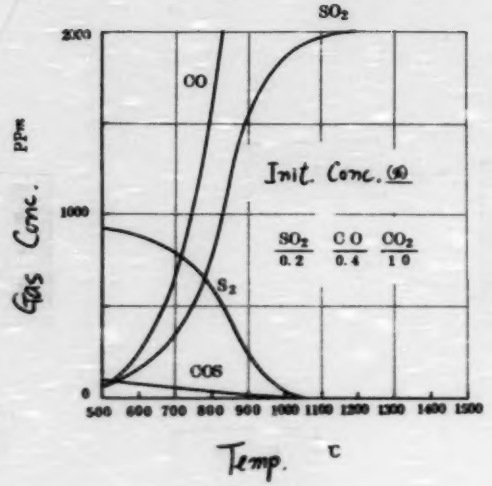

Fig. A7. Gas composition in equilibrium (CO: 0.4%; CO_2: 10%)

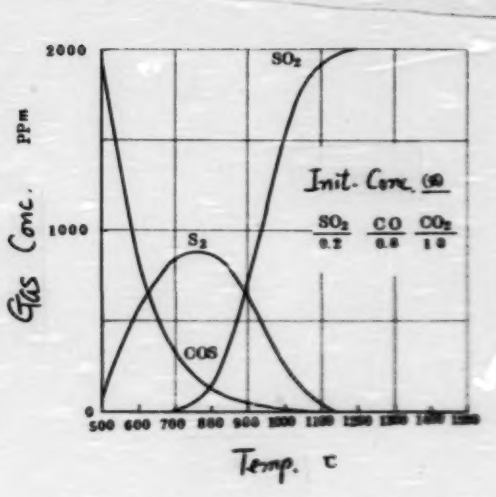

Fig. A8. Gas composition in equilibrium (CO: 0.8%; CO_2: 10%)

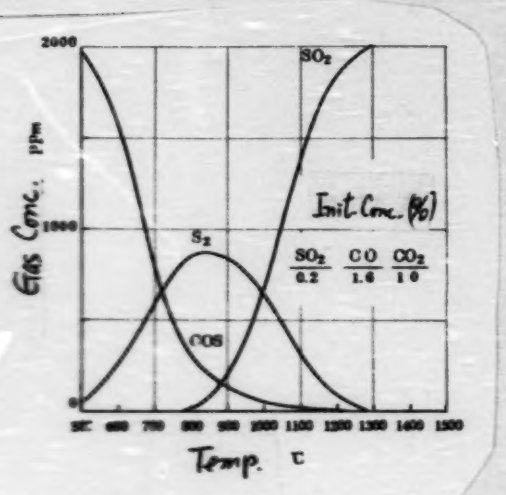

Fig. A9. Gas composition in equilibrium (CO: 1.6%; CO_2: 10%)

一酸化炭素による二酸化いおうの接触還元

(第Ⅰ報　二酸化いおう変化率に対するガス濃度の影響)

福澤　久[※]　石原義巳[※※]

昭和47年3月30日

Catalytic Reduction of Sulfur Dioxide by Carbon Monoxide

(Part I. Effect of Gas Concentrations on the Conversion of Sulfur Dioxide)

by Hisashi Fukuzawa and Yoshimi Ishihara

Synopsis

The thermodynamics and the kinetics of catalytic sulfur dioxide reduction by carbon monoxide in the gas mixture consisted of sulfur dioxide, carbon monoxide, carbon dioxide and nitrogen were investigated in this paper.

(1) The maximum conversion of sulfur dioxide was obtained at 400~500 ℃ by using bauxite as a catalyst.

(2) The catalysts having metal oxides such as iron, copper, calcium and silver in each alumina showed high activity on the sulfur dioxide reduction by carbon monoxide.

(3) The equilibrium conversion of sulfur dioxide by carbon monoxide increased with the increase of the reaction temperature and carbon monoxide concentration but decreased with the increase of carbon dioxide concentration.

(4) The reaction rate by bauxite catalyst had first-order dependence on sulfur dioxide concentration and carbon monoxide concentration but was affected inversely by carbon dioxide concentration at temperatures above 600 ℃.

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要　　旨

排煙脱硫の一手段として，一酸化炭素による二酸化いおう直接還元法の可能性を探究するために種々の実験条件下において検討した。

本報告は，固定床式実験装置を用い，$SO_2 - CO - CO_2 - N_2$ 系混合ガス中における二酸化いおうと一酸化炭素との反応速度および化学平衡について考察したものである。

(1) ガス中に高濃度の二酸化炭素が含まれる場合に，４００～５００℃の温度域でもっとも高い二酸化いおう変化率が得られた。

(2) 鉄，銅，カルシウムおよび銀をそれぞれ担持させたアルミナ触媒は高い活性を示し，ボーキサイトは鉄を担持させたアルミナ触媒と同程度の高い活性を示した。

(3) 平衡状態における二酸化いおう変化率は，反応温度の低下および一酸化炭素濃度の増加とともに高くなり，二酸化炭素濃度の増加とともに低下する。

(4) ボーキサイトを触媒とした場合の反応速度は二酸化いおう濃度および一酸化炭素濃度に比例して増加したが，６００℃以上の温度域では二酸化炭素濃度の増加とともに減少した。

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1　まえがき

排煙脱硫法の研究開発は，日本，ドイツ，アメリカ，フランスなどの各国で種々の方法について進められているが，まだ実用可能な方法は確立されていない。

一酸化炭素による二酸化いおうの直接還元法は，つぎに示す化学反応によって二酸化いおうを元素いおうに還元することができる。

$$SO_2 + 2CO = 1/2\ S_2 + 2CO_2$$

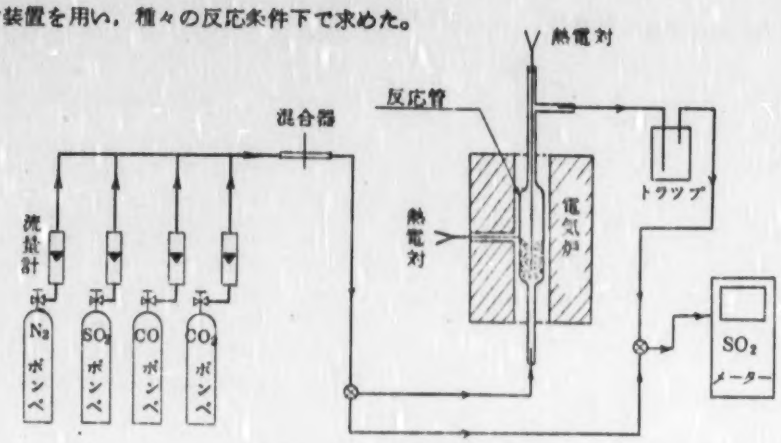
本方式に関して，カナダのR. Lepsoe は二酸化いおう還元反応を熱力学的に考察して報告しており，[1] また焙焼炉排ガスを対象に反応温度２５０～７００℃，接触時間６０秒の条件下で主として活性アルミナ触媒（その他の触媒については不明である）の活性を比較している。[2] また，燃焼炉排ガスを対象にアメリカのP. R. Ryason らは反応温度５４０℃，接触時間０３５秒の条件下で二酸化いおうを０５％含む$SO_2 - CO - CO_2 - N_2$からなる合成ガスを用いて各種触媒（銅，銀およびパラジウムをそれぞれ担持させた触媒，銅，銀，ニッケルおよびマグネシウムをそれぞれ担持させたシリカ触媒）の活性を比較している。[3] 最近では燃焼炉排ガスを対象にMassachusetts 大学により酸素を含まないガスを用いて活性触媒が探索研究されているが，[4] まだ詳細は報告されていない。さらにSanaa E. K-halafalla らにより$SO_2 - CO - N_2$からなる合成ガスを用いて反応温度５００～６００℃における二酸化いおう除去率に対する鉄－アルミナ触媒中の鉄含有量の影響について報告されている。[5]

本研究は燃焼炉排ガス中の二酸化いおうの一酸化炭素による直接還元法の可能性を明らかにするため，固定床式小型実験装置により$SO_2 - CO - CO_2 - N_2$からなる合成ガスを用い反応温度１００～９００℃，接触時間０３０秒以下の条件下で触媒効果（主としてボーキサイト）の検討と反応速度および化学平衡について考察を行なったものである。

2 実験方法

2.1 実験装置と実験方法

$SO_2 - CO - CO_2 - N_2$ 系混合ガス中における二酸化いおうと一酸化炭素との反応の速度は，第1図に示す装置を用い，種々の反応条件下で求めた。



第1図　実験装置

本装置の石英製反応管は，内径2.7cm，長さ105cmである。

供試混合ガスは，二酸化いおう標準ガス（SO_2　0.5%，窒素バランス），一酸化炭素標準ガス（CO　100%，窒素バランス），二酸化炭素（CO_2　99.9%）および窒素をそれぞれのボンベから所定量を流通させ，混合して調製した。なお，均一に混合させるために内径0.04cmのガラス製オリフィスを通過させた。

反応管中の触媒層を通過する間に混合ガス中の二酸化いおうと一酸化炭素とが反応して，二酸化いおうは元素いおうに還元され，二酸化いおう濃度が減少する。反応前後の二酸化いおう濃度を導電率型二酸化いおう濃度計で測定し，その濃度差から二酸化いおう変化率を求めた。また，一酸化炭素濃度および二酸化炭素濃度は，ガスクロマトグラフィーにより適時測定した。

なお，つぎの実験条件を基準として，それぞれの影響を検討した。

実験条件

i.	二酸化いおう濃度	0.17～0.19%
ii.	一酸化炭素濃度	0.4～1.6%
iii.	二酸化炭素濃度	0～1.5%
iv.	ガス流量	0.25～1.5 l/min
v.	反応温度	100～900℃
vi.	触媒充填量	0～20 ml

触媒充填時の空間速度は約1,000～30000h^{-1}（NTP）であり，その時の接触時間は約002～030秒である。

2.2 供試触媒

供試触媒として粒径20～40㎜の

第1表　活性アルミナおよびボーキサイトの化学組成

3. 実験結果

3.1 無触媒の場合

何も充填しない反応管内に二酸化いおう0.17～0.19%，一酸化炭素0.4～1.6%の範囲内の所定濃度に調節した混合ガスを0.25 l/min で流通させ，反応温度500～900℃の範囲で一酸化炭素による二酸化いおうの還元実験を行なった。得られた結果を第2図に示す。

SO_2 残存率

温度 ℃

第2図　無触媒の場合の二酸化いおう変化率

同図からわかるように，触媒のない場合には二酸化いおうは一酸化炭素によってほとんど還元され

ず，反応温度９００℃の場合でも二酸化いおうの変化率は５％程度に過ぎなかった。一酸化炭素濃度を二酸化いおう濃度の２～８倍の範囲で変化させても，二酸化いおう変化率はほとんど変らなかった。

活性アルミナを用いた場合の二酸化いおう変化率

化いおう率が得られることを示している。

それぞれ活性アルミナに金属として５ wt％

１８～０１９％，一酸化炭素濃度０８％，二酸

，空間速度５０００～３００００ h^{-1} ）で流通

した場合の二酸化いおう変化率を第４～６図

二酸化炭素の存在の有無にかかわらず，マグネ

う変化率が活性アルミナの場合の約３倍に増加した。触媒効果の大きい鉄を担持させたアルミナの場合は一酸化炭素濃度が二酸化いおう濃度の４倍，反応時間０１３秒以上で８０％以上の二酸化いおう変化率が得られた。

また，第６図から明らかなように，金属を担持させたアルミナを触媒とした場合に二酸化いおう変

化率は４００～６００℃でもっとも高くなり，４００℃以下では反応温度の低下とともに，また，６００℃以上では反応温度の上昇とともに低下した。

R. Lepsoe[2]は反応温度２５０～７００℃，接触時間６０秒の反応条件下で活性アルミナなどの各種触媒の活性を比較しているが，その詳細については報告されていない。また，Sanaa E. Khalafallaら[3]は，アルミナに赤鉄鉱を添加した触媒を用いて，反応温度５００℃，二酸化いおう濃度４７%，一酸化炭素濃度１０%，窒素バランス，ガス流量０５～２０ℓ/minの反応条件下で触媒中の鉄含有量の影響を検討し，鉄含有率が４３%の時にもっとも高い活性を示すと報告している。

P. R. Ryasonら[3]は，二酸化いおう濃度０５%，一酸化炭素濃度２０%，二酸化炭素濃度１０%，窒素バランスの混合ガスを流通させ，反応温度５４０℃，接触時間０３５秒（空間速度１０４h^{-1}）の反応条件下で，また，Massachusetts大学[4]では，酸素を含まない混合ガスを流通させ，反応温度５００℃以下の反応条件下でそれぞれ触媒の検討を行ない，いずれも銅－アルミナ触媒がもっとも活性であると報告しており，本実験とは若干反応条件が異なるが，活性の高い物質の種類についてはほぼ同様な結果が示されている。

第４図　二酸化いおう変化率に対する担持金属の影響
（その１－CO　0.8%の場合）

第５図　二酸化いおう変化率に対する担持金属の影響
（その２－CO　0.8%，CO_2　10%の場合）

第6図　二酸化いおう変化率に対する担持金属の影響
（その3－CO 0.8%，CO_2 10%の場合）

濃度0.18～0.19%，一酸化炭素濃度
ガスを0.3～2.0 l/min（空間速度5000
900℃における二酸化いおう変化率を第

変化率は，第7図からわかるように，活性ア
一酸化炭素濃度の増加，反応温度の上昇およ
トは，鉄あるいは銅を担持させたアルミナ触
生を示し，一酸化炭素濃度が二酸化いおう濃
00 h^{-1} 以下で70%以上の二酸化いおう変

化率は，第8～10図からわかるように，鉄
でもっとも高くなり，300℃以下では反応温度の低下，600℃以上では反応温度の上昇，一酸化炭素濃度の減少，二酸化炭素濃度の増加および空間速度の増加とともに低下した。

以上の二酸化いおう変化率が得られることを示している。

硫化カーボニル（COS）の生成量は第１３図および付図４～６に示したガス組成の試算例から明らかなように，一酸化炭素濃度が二酸化いおう濃度の２倍の場合には，５００～１０００℃の温度域で１０ppm 程度まで生成すると考えられることを示している。また，４倍以上の場合には，１０００℃以上で１０ppm 程度まで，１０００℃以下では温度の低下とともに生成量は急激に増加すると考えられることを示している。

(2) 反応前のガス中に二酸化炭素を含む場合

ガス中に二酸化炭素を含む場合の二酸化いおう変化率は第１２図に一例を示したように，反応温度の低下，一酸化炭素濃度の増加および二酸化炭素濃度の減少とともに急激に高くなることがわかる。

重油燃焼排ガス中には二酸化炭素が１２～１５％含まれるが，第１２図および付図１～３から，ガス中の二酸化炭素濃度が１０～１５％の場合に理論上６０％以上の二酸化いおう変化率を得るためには，一酸化炭素濃度が二酸化いおう濃度の２倍の場合は７８０℃以下，４倍の場合は９００℃以下，８倍の場合は１０００℃以下にすればよいことがわかる。

また，平衡状態におけるガス組成の試算例を第１４図に示す。ガス中に１０～１５％の二酸化炭素が含ま

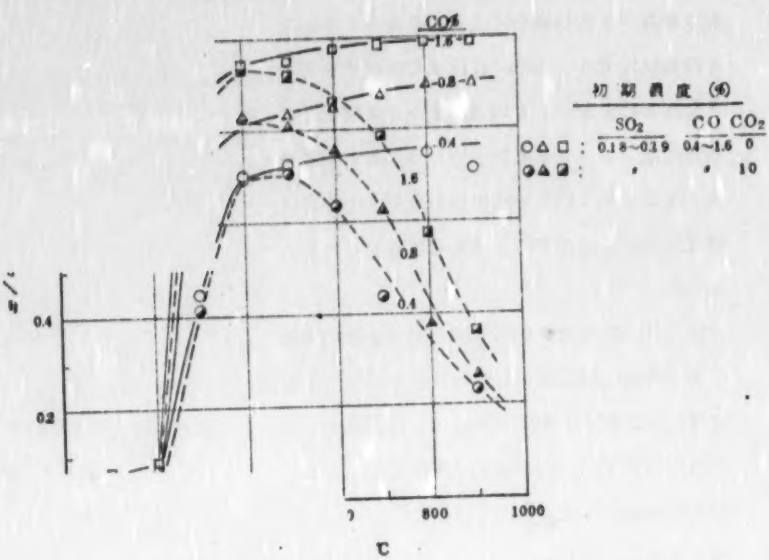
温　度　℃

第１３図　平衡状態におけるガス組成
（その１－CO 0.5％の場合）

温度 ℃

第１４図　平衡状態におけるガス組成
（その２－CO 0.5％，CO_2 10％の場合）

化いおう変化率が得られる条件下において，硫化カーボ
（二酸化いおう初期濃度が２０００ppmの場合には４０
また，同図および付図７～９に示したように一酸化炭素
は，８００℃以下では温度の低下とともに硫化カーボニ



ように反応前のガス中に二酸化炭素が含まれず，一酸化炭素濃度が０８％以上であれば反

率の実測値と平衡値の比と

の場合）

，っとも有利と考えられる４００～５００
衡値の６０％以上の二酸化いおう変化率

変化率が得られる反応温度域は触媒の種類を担持させたアルミナで５００℃，銀を担持させたアルミナで６００℃，カルシウムを担持させたアルミナで５００℃，活性アルミナで５００℃，ボーキサイトで４００℃であった。

活性アルミナに金属を担持させた触媒の活性は，第４～６図から明らかなように，鉄－銅－カルシ

ウム－銀の順序でほゞ同程度の高い活性を示し，二酸化いおう変化率は活性アルミナのみの場合の約2～4倍であった。また，マグネシウムは活性を示さなかった。

触媒の担体として用いた活性アルミナおよびボーキサイトの比表面積と細孔容積を第2表に，細孔容積と細孔半径との関係を第16図に示す。平均細孔半径がほゞ等しく，比表面積と細孔容積はボーキサイトよりも活性アルミナの方が大きかったが，ボーキサイトは活性アルミナにくらべて鉄を担持させたアルミナと同程度の高い活性を示した。これはボーキサイト中の鉄の触媒効果が大きいためと考えられる。

すなわち，一酸化炭素による二酸化いおうの還元反応は活性金属の触媒効果によるところが大きいと考えられる。

第2表　活性アルミナおよびボーキサイトの比表面積と細孔容積

触　媒	粒　径	真密度	充塡密度	比表面積	細孔容積	平均細孔半径
焼成活性アルミナ						
焼成ボーキサイト						

細孔容積 cm³/g

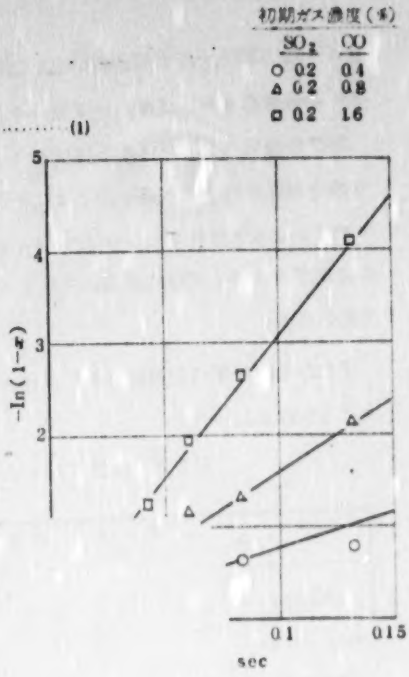
第16図

4.3 反応速度式

二酸化いおうと一酸化炭素との反応式は

$$SO_2 + 2CO = \frac{1}{2} S_2 + 2CO_2 \quad \cdots\cdots (1)$$

で示され，ボーキサイトを触媒とした場合の反応速度は第17図に示すように二酸化いおう分圧に関して一次であった。また，同図の勾配は一酸化炭素の濃度に比例しているので，一酸化炭素分圧に関しても一次であった。しかし，一酸化炭素に関しては300℃以下で，二酸化炭素に関しては600℃以上でそれぞれの分圧の増加とともに反応速度が減少する傾向が認めら



時間との関係
(700℃)

い

場を

い

の温度

=0と

二酸化

る。

93式を積分して変数分離し，反応速度定数 k を次式

$$k = A + \beta B \qquad \cdots\cdots 95$$

で表わす。

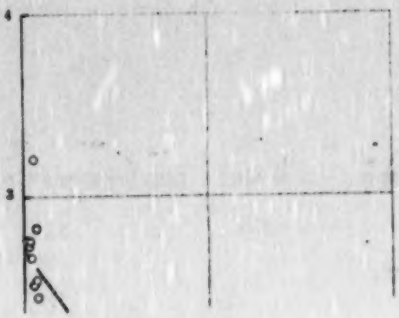
第3表　実験結果一覧表　（触媒：ボーキサイト，700℃）

	ガス流量	接触時間	SO_2 分圧	CO 分圧	CO_2 分圧	SO_2 変化率	SO_2 平衡変化率

第3表の実験結果を93式に代入，整理してAとBとの関係を第18図に示す。同図からわかるように多少のバラツキはあるが直線で表わすことができ，その切片と勾配から k と β を求めることができる。また，400～900℃の各温度についても同様に整理することができた。すなわち，400～900℃の温度域での反応速度は二酸化いおう分圧，一酸化炭素分圧に比例して増加したが，二酸化炭素分圧の増加とともに減少し，99式で表わすことができた。

また，300℃以下の温度域における反応速度式を同様にして吟味すると，この温度域では二酸化炭素の触媒への吸着による反応速度に対する影響が極めて小さく，99式で $\beta P_{CO_2} \fallingdotseq 0$ となるために，βP_{CO_2} 項を無視することができた。すなわち，300℃以下の温度域での反応速度は二酸化いおう分圧，一酸化炭素分圧に比例して増加するが，一酸化炭素の触媒への吸着による影響をうけ，次式で表わすことができた。

$$\cdots\cdots 00$$



以上を要約すると，３００～９００℃の温度域での反応速度は，二酸化いおう分圧，一酸化炭素分圧に比例すること，また，一酸化炭素分圧，二酸化炭素分圧の増加にともない，触媒への吸着による速度阻害があること，などにより一般

$$-\frac{dP_{SO_2}}{dt} = k\frac{P_{SO_2}P_{CO}}{1+\beta P_{CO_2}} \qquad \cdots\cdots(1)$$

4.4 反応速度におよぼす諸因子の影響

4.4.1 反応温度の影響

ボーキサイトを触媒とした場合の反応速度定数 k，定数 α，β と反応温度との関係を第１９図に示す。

同図から明らかなように，一酸化炭素の触媒への吸着の大きさを表わす α は３００℃以下の温度域で，また二酸化炭素の触媒への吸着の大きさを表わす β は６００℃以上の温度域で著しく大きくなり，減速効果が大きかった。また，４００～５００℃の温度域では一酸化炭素および二酸化炭素の触媒への吸着による減速効果は極めて小さかった。すなわち，反応速度は低温域で一酸化炭素，高温域で二酸化炭素の影響をうけるが，反応温度の上昇とともに除々に

反応速度定数 k をArrhenの式にしたがって整理し，

(Arrheniusの式) 09

見掛けの活性エネルギーを求めると約3 Kcal，mol^{-1} であり，k は次式

$$k = 16\times10^{4}\,e^{-3100/kT} \quad \cdots\cdots 07$$

で表わすことができた。

4 4 2 一酸化炭素濃度の影響

ボーキサイトを触媒とした場合の二酸化いおう変化率に対する一酸化炭素の影響を第9図に示したように，反応温度７００℃，二酸化いおう濃度０１８～０１９％，二酸化炭素濃度１０％，空間速度５０００h^{-1} の時の二酸化いおう変化率は，一酸化炭素濃度が０４％の場合に３６％，０８％の場合に６２％，１６％の場合に７４％であった。また，第１９図に示したαと

第１９図　k，αおよびβと温度との関係

反応温度との関係から明らかなように，３００℃以下の温度域では一酸化炭素の触媒への吸着による減速効果が大きいが，４００℃以上の温度域では一酸化炭素による減速効果は極めて小さかった。すなわち，反応速度は，３００℃以下の温度域では一酸化炭素の触媒への吸着により減速されるが，反応温度の上昇および一酸化炭素濃度の増加とともに速くなった。

素濃度の影響を第１０図に

れない場合に８８％，濃度が5

あった。また，第１９図に示し

では二酸化炭素の触媒への吸着

炭素による誘導効果が著しく大

化炭素の触媒への吸着により減

くなった。

文と同様にArrheniusの式に

は次式

酸化炭素との反応速度を種々の

は５％以下であったが，触媒を

中に高濃度の二酸化炭素が含まれ

おう変化率が得られた。

ルシウム，銀が高く，マグネシウムは活性を示さなかった。また，ボーキサイトは鉄触媒と同程度の高い活性を示した。

(3) 平衡状態における二酸化いおう変化率は，反応温度の低下および一酸化炭素濃度の増加とともに高くなり，二酸化炭素濃度の増加とともに低下する。ガス中に１０～１５％の二酸化炭素が含まれる場合に，一酸化炭素濃度が二酸化いおう濃度の２倍の場合は６２０℃以下，４倍の場合は８００℃以下，８倍の場合は９００℃以下で理論上９０％以上の二酸化いおう変化率が得られる。

(4) ボーキサイトを触媒とした場合の反応速度は二酸化いおう濃度および一酸化炭素濃度に比例して増加したが，６００℃以上の温度域では二酸化炭素濃度の増加とともに減少した。

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8. 付　録

一酸化炭素による一酸化ニッケルの還元反応の平衡状態における一酸化ニッケルの化学とガス組成の試算例

1　反応式

初　濃

平衡時濃

K

初　濃

平衡時

$$\cdots \quad [CO][S_2]^{1/2} \qquad (9)$$

ただし，XおよびYは平衡変化率である。

R.Lepsoe によれば平衡定数（K_1，K_2）と温度の関係は次式で示され，

K_1 , K_2 と温度との関係を第１１図に示した。

ii 平衡時におけるガス濃度

	初濃度	平衡時濃度
〔CO〕	a	$a(1-X-Y)$
〔SO_2〕	b	$b-\frac{a}{2}X$
〔CO_2〕	c	$c+aX$
〔S_2〕	0	$\frac{a}{4}(X-2Y)$
〔COS〕	0	aY

ここで，a＝０４，０８，１６％，b＝０２％，c＝０，５，１０，１５％の場合の二酸化いおう変化率を付図１～３に，ガス組成の一例を付図４～９に示す。

付図１　平衡状態における二酸化いおう変化率

（その１－CO ０４％の場合）

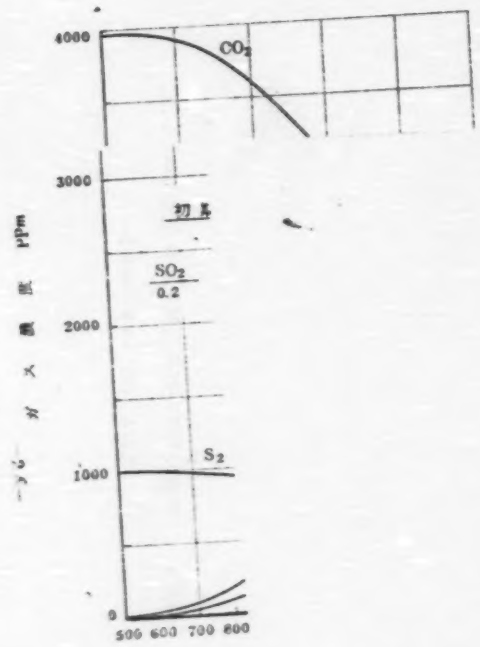
SO_2 conversion rate in equilibrium state

付図 2　　平衡状態における二酸化いおう変化率

（その2－CO 0.8％の場合）

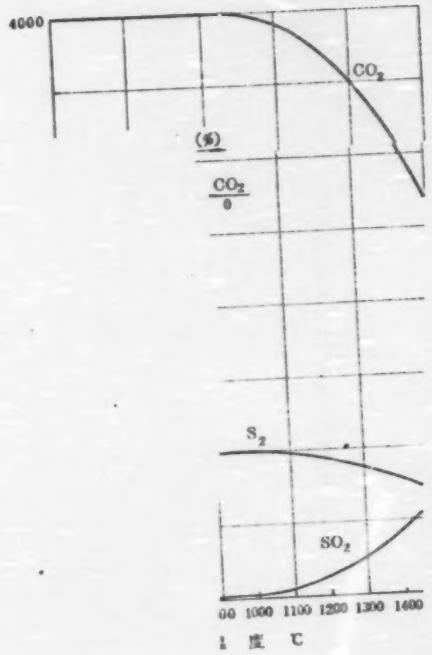
付図 3　　平衡状態における二酸化いおう変化率

（その3－CO 1.6％の場合）



付図 4　平衡状態におけるガス組成

（その 1 － CO 0.4％の場合）



付図 4　平衡状態におけるガス組成

（その 2 － CO 0.8％の場合）

成

（その 3 － CO 1.6％の場合）

付図7　平衡状態におけるガス組成
（その4－CO 0.4%，CO_2 10%の場合）

付図8　平衡状態におけるガス組成
（その5－CO 0.8%，CO_2 10%の場合）

付図9　平衡状態におけるガス組成
（その6－CO 1.6%，CO_2 10%の場合）